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RESEARCH ARTICLE

Biochar organic fertilizers from natural resources as substitute for mineral fertilizers

Bruno Glaser · Katja Wiedner · Sebastian Seelig · Hans-Peter Schmidt · Helmut Gerber

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Abstract Biochars are new, carbon-rich materials that could sequester carbon in soils improve soil properties and agronomic performance, inspired by investigations of Terra Preta in Amazonia. However, recent studies showed contrasting performance of biochar. In most studies, only pure biochar was used in tropical environments. Actually, there is little knowledge on the performance of biochar in combination with fertilizers under temperate climate. Therefore, we conducted an experiment under field conditions on a sandy Cambisol near Gorleben in Northern Germany. Ten different treatments were established in 72-m^2 plots and fivefold field replicates. Treatments included mineral fertilizer, biogas digestate, microbially inoculated biogas digestate and compost either alone or in combination with 1 to 40 Mg ha^{-1} of biochar. Soil samples were taken after fertilizer application and maize harvest. Our results show that the biochar addition of 1 Mg ha^{-1} to mineral fertilizer increased maize yield by 20 %, and biochar addition to biogas digestate increased maize yield by 30 % in comparison to the corresponding fertilizers without biochar. The addition of 10 Mg ha^{-1} biochar to compost increased maize yield by 26 % compared to pure compost. The addition of 40 Mg ha^{-1} biochar to biogas digestate increased maize yield by 42 % but reduced maize yield by 50 % when biogas digestate was fermented together with biochar. Biochar-fertilizer combinations increased K, Mg and Zn and reduced Na, Cu, Ni and Cd uptake into maize. Overall, our findings demonstrate that biochar-fertilizer combinations have a better performance than pure fertilizers, in terms of yield and plant nutrition. Therefore, an immediate substitution of mineral fertilizers is possible to close regional nutrient cycles.

Keywords Water holding capacity · Plant nutrition · Mineral fertilizer · Biogas digestate · Compost · Effective microorganisms · Central Europe · Microbial inoculation · Temperate climate conditions · Biochar organic fertilizer interaction

1 Introduction

Large areas of Northern Germany were influenced by Quaternary glaciations descending from Scandinavia, leading to extensive glacial outwash plains and leaving behind soils characterized by a sandy texture with low nutrient and soil organic matter contents and with low nutrient and water holding capacities. Agriculture in Northern Germany is limited by low soil fertility and is prone to extreme weather events such as heavy rain and extended drought periods. Current climate conditions in many parts of the northern German inland yield low precipitation (<600 mm). According to climate predictions for the Wendland region (Northern Germany), the temperature will increase by 1.1 °C until 2050 and by 2.9 °C until 2100. Precipitation will be subject to strong seasonal fluctuations with an increase of 30–40 % in winter and a decrease of 40–50 % during the growing season (Lavalle et al. 2009).

In recent years, carbon-rich biomass carbonization products, also known as biochar, have become increasingly the subject of scientific and public interest. It is claimed that biochar can improve soil properties and agronomic performance, inspired by investigations of Terra Preta in Amazonia (Glaser and Birk

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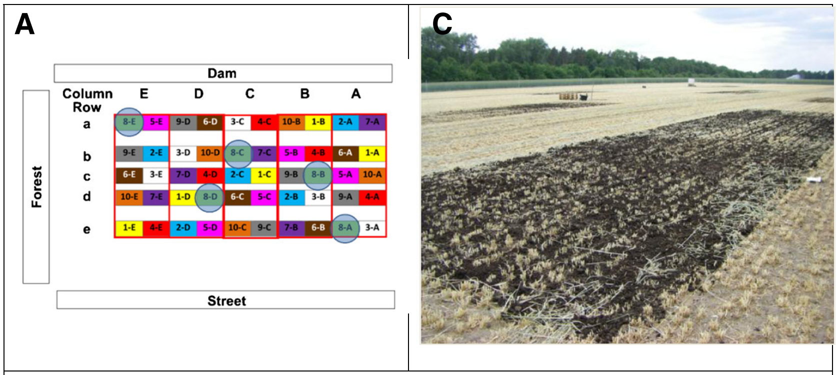
2012). Several studies showed that the biochar application to soil can influence soil properties, e.g. water holding capacity, pH or microbial activity (Atkinson et al. 2010; Glaser et al. 2002). Further studies observed enhanced nutrient uptake by plants after biochar application (Lehmann et al. 2003). In contrast, some authors reported no significant effects of biochar on soil properties, plant nutrition or biomass production after biochar application under field conditions (Major et al. 2010). Until now, most biochar studies were performed with pure biochar under laboratory or greenhouse conditions or under tropical environments (Jeffrey et al. 2011). Biochar studies under field conditions often show contrasting results to those conducted in the laboratory (Liu et al. 2013). In addition, variation due to heterogeneous site conditions is much higher but, of course, is more realistic. Therefore, experiments under field conditions with agronomically relevant fertilizer types and amounts better reflect realistic conditions with respect to response of agricultural ecosystems differing in soil properties, weather conditions and agricultural processing methods.

In this study, we conducted a field experiment to quantify the effects of biochar on soil and plant properties when combined with agronomically relevant inorganic and organic fertilizers (Fig. 1). To be as realistic as possible, we collected organic feedstock to produce organic fertilizers on the farm and selected the plots for the field trial as big as possible (Fig. 1). We chose maize in the first year of the field experiment for two reasons: it is (i) a nutrient-demanding plant and (ii) an economically important plant, especially used for biogas production. Commercial mineral fertilizer was used as a control and biogas digestate and compost from regional resources were used in quantities to achieve a plant-available N level of 200 kg N ha^{-1} (Fig. 1). Biochar was used in two different amounts according to the following considerations. On a different sandy soil in north-eastern Germany, plant growth increased with an increase in the amount of biochar (Liu et al. 2012), and the highest biochar amount was 20 Mg ha^{-1}. Therefore, we chose 40 Mg ha^{-1} to find out if the positive results of Liu et al. (2012) can further be improved. However, considering the current market value of biochar of about 500 € per ton and the production capacity of a PYREG reactor of about 400 Mg biochar per year, a repeated annual application of low biochar amount might be economically feasible for agricultural holdings. Applying e.g. 1 Mg ha^{-1} per year, a total area of about 400 ha could be treated with biochar annually if one PYREG reactor is available.

2 Material and methods

2.1 Location

Established in May 2012, the field trial is located near Gorleben at 53° 01′ 09.26″ N and 11° 29′ 50.04″ E 19 m above sea level in the Wendland region of Lower Saxony, Germany. Mean annual precipitation is 575 mm, and mean annual temperature



Column Row	E		D		C		B		A	
a	8-E	5-E	9-D	6-D	3-C	4-C	10-B	1-B	2-A	7-A
b	9-E	2-E	3-D	10-D	8-C	7-C	5-B	4-B	6-A	1-A
c	6-E	3-E	7-D	4-D	2-C	1-C	9-B	8-B	5-A	10-A
d	10-E	7-E	1-D	8-D	6-C	5-C	2-B	3-B	9-A	4-A
e	1-E	4-E	2-D	5-D	10-C	9-C	7-B	6-B	8-A	3-A

B

Fertilizer	N [kg N ha^{-1}]	Biochar [Mg ha^{-1}]	Indigeneous microorganisms	Treatment
Mineral	200	n.a.	n.a.	Mineral fertilizer
Mineral	200	1	n.a.	Biochar 1 mineral fertilizer
Mineral	200	40	n.a.	Biochar 40 mineral fertilizer
Maize digestate	200	n.a.	n.a.	Digestate
Maize digestate	200	1	n.a.	Biochar 1 digestate
Maize digestate	200	40	n.a.	Biochar 40 digestate
Maize digestate	200	n.a.	yes	Fermented digestate
Maize digestate	200	40	yes	Biochar40 fermented digestate
Compost	200	n.a.	n.a.	Compost
Compost	200	10	n.a.	Composted biochar

Fig. 1 **a** Field experiment using a Latin rectangle statistical design with ten different treatments (*1–10*) and five replicates (*A–E*). Each treatment occurs only once in each row and column, indicated by *circles* around treatment 8. **b** Overview of individual treatments, *n.a.* not amended. **c** Individual plots size is 6×12 m with a total area of 72 m^2. Total size of the field trial is 3600 m^2

is 8.8 °C. Total precipitation was 231 mm and mean air temperature 16.6 °C during our experiment from 30 May 2012 to 24 September 2012 (www.dwd.de).

2.2 Experimental design

The large-scale field trial was arranged according to a Latin rectangle (Richter et al. 2009), which includes ten different treatments (1–10) with five replicates (A–E) and so comprises 50 plots each 6 m × 12 m. Figure 1 illustrates schematically the chosen structure and the assignment of treatments within the Latin rectangle. Between the rows, corridors were left, which enabled access to the individual plots without disturbing neighbouring plots (Fig. 1a). These tracks were also used for agricultural machines and irrigation systems (Fig. 1a). Each plot is subdivided into a core plot, which is flanked by 2 m margins to both ends in lateral direction and 2.5 m margins in longitudinal direction. The core plots are 2 × 7 m in dimension from which all samples were taken.

Commercially available mineral fertilizer, biogas digestate, biogas digestate inoculated with indigenous microorganisms extracted from adjacent forest soil and on-farm produced compost made from regional resources were used as fertilizers on a fixed N level of 200 kg ha^{-1} and mixed with different amounts of biochar (Fig. 1b). A cultivator was used to incorporate the fertilizers into the top 15 cm soil depth.

Biochar was made from green cuttings, produced in a PYREG™ reactor at ~650 °C (Dörth, Germany, www.pyreg.de). Detailed information about the PYREG™ technology and the used biochar is described in Wiedner et al. (2013). Material properties of biochar were as follows: pH 10.3, electrical conductivity 292 µS cm^{-1}, ash content 23 %, total carbon content 66.7 %, total nitrogen content 3 %, total oxygen content 5.7 % and total hydrogen content 1.1 % (Wiedner et al. 2013).

Mineral fertilizer consisted of 16.15 kg potassium oxide with magnesium oxide, 5.26 kg diammonium phosphate and 13.6 kg urea with 46 % N. Biochars 1 and 40 treatments received 1 and 40 Mg ha^{-1}, respectively, on a dry matter basis. For the biochar 1 mineral fertilizer treatment, the mineral fertilizer was diluted in warm water and biochar was added to soak up the liquid containing the fertilizer. For the biochar 40 mineral fertilizer treatment, biochar was mixed only with the mineral fertilizer granules without water.

Biogas digestate from maize was provided by a commercial biogas plant of the region (Biogas Gartow GmbH & Co. KG, Gartow, Germany). For each corresponding treatment, 1368 L of pure digestate was distributed on the five replicate plots, corresponding to 30 m^3 per hectare, an amount typical for the Wendland region. For biogas digestate mixed with 1 and 40 Mg ha^{-1} biochar, 1368 L of biogas digestate was mixed with 48 and 1920 kg biochar with 75 % dry matter content, respectively. These mixtures were distributed to the five field replicates (72 m^2 each).

To test whether microbial inoculation has additional beneficial effects, we inoculated biogas digestate with indigenous microorganisms extracted from adjacent forest soils. For this purpose, 500 L of digestate was mixed with 100 L indigenous microorganism stock solution, 15 L molasses, 15 L maize silage and 60 L water. Two days later, 870 L digestate, 30 L molasses, 30 L water and 1920 kg biochar (dry matter 75 %) were added. The same mixture was also prepared without biochar, and the two mixtures were spread to the five corresponding field replicates with and without 40 Mg ha^{-1} biochar corresponding to 200 kg N ha^{-1}.

Compost was produced at industrial scale, outdoor and under practical field conditions with locally available resources at full exposure to weather conditions near the field experiment. Compost components were green cutting biochar (0.7 Mg), straw (1.1 Mg), draff (5.3 Mg), horse manure (1.1 Mg), maize silage (5.3 Mg), loam (5.3 Mg) and stone powder (0.017 Mg). Within 45 days of composting, the compost pile was turned seven times. Biochar was mixed to half of the fresh organic material prior to composting, corresponding to 10 Mg ha^{-1} in the final mixture.

Kalvin silage maize (ID 12835) was sown directly after fertilization at the end of May 2012 and was harvested at the end of September 2012. No irrigation was given to crops during the growing season. Appropriate combinations of herbicides and fungicides were applied to control weeds and fungi.

2.3 Soil sampling and analysis

Soil samples were taken between 0 and 15 cm depth of the core plots directly after fertilization and harvest. Electrical conductivity and pH of soil samples and fertilizers were measured using suspensions with 0.01 M $CaCl_2$ and distilled H_2O at a soil to solution ratio of 1 to 5. After shaking the suspensions for 1 h on a low-speed shaker and sedimentation of solids for another hour at room temperature, pH and electrical conductivity were determined in the supernatant. Exchangeable cations were analysed according the method of Trueby and Aldinger (1989) using 0.5 M NH_4Cl for extraction and inductively coupled plasma optical emission spectroscopy for quantification. For plant-available phosphate extraction, 2.5 g of soil was shaken with 0.5 M $NaHCO_3$ at pH 8.5 for 30 min according to Olsen et al. (1954). The extracts were analysed using a segmented flow analyser (San^{++} Skalar Analytical). Total N contents of maize plants and soil were measured using a Euro EA Elemental Analyser (EuroVector, Hekatech, Germany). Mineral N (NH_4^+ and NO_3^-) was extracted from fresh soil samples with 1 M KCl and analysed using a segmented flow analyser (San^{++} Skalar Analytical). To evaluate the water holding capacity, 10 g of soil sample was weighed into plastic cylinders with fine-mesh strain on the bottom and was placed in water. After 24 h, saturated samples were drained until water release stopped and were weighed again for calculation of water holding capacity.

2.4 Maize sampling and analysis

Before maize harvest, 32-m^2 subplots within each plot were marked and all maize plants were counted. After cutting and weighing of the plants, ten maize plants were selected randomly, chaffed and weighed again. After homogenization, random samples were taken and dried to a constant mass at a temperature of 65 °C and were ground for further analysis. For multi-element analysis of maize plants, 150-mg ground plant material was weighed into 20-mL Teflon digestion tubes. Two millilitres of concentrated nitric acid, 0.8 mL H_2O_2 and 2.5 mL high purity water were added. Then, an automated microwave digestion was carried out (MARS Xpress 5, CEM). Vessels were heated at 180 °C for 20 min. After cooling, liquids were filtered through ash-free filters into 10-mL volumetric flasks. Volumetric flasks were filled up with high purity water. Diluted samples were analysed using an inductively coupled plasma optical emission spectrometer (ULTIMA 2, HORIBA Scientific S.A.S., Jubin-Yvon, France).

2.5 Statistical analysis

Data were analysed using SPSS® Statistics 21 software (SPSS Inc., Chicago, USA). We used two statistical procedures. First, a linear mixed effects model was applied taking advantage of the special design of our field experiment. Each treatment occurs exactly one time in each row and in each column (Fig. 1a) so that the column and the row could be used as either fixed or random effects. However, it turned out that this procedure did not reveal any advantage over simpler statistical models. Therefore, we preferred using ANOVA with Tukey's HSD as post hoc test. In all cases, level of significance was $p<0.05$.

3 Results and discussion

3.1 Fertilizer effects on soil properties

Compost application revealed about 50 % higher water holding capacity compared to mineral fertilizer and biogas digestate (Fig. 2a). This effect is well known (Fischer and Glaser 2012; Liu et al. 2012; Shiralipour et al. 1992) and can be explained by lowering bulk density and thus increasing soil porosity. Such is especially useful for soils with low water holding capacity, such as the sandy soils in the study region in combination with high precipitation followed by longer drought periods (Liu et al. 2012).

Mineral fertilizer had the lowest pH in comparison to biogas digestate and compost (Table 1). Right after fertilization in May 2012, this effect was still obvious in soil (Table 1), but after one vegetation period in September 2012, soil pH was more or less homogeneous among all pure fertilizer treatments (Table 1). This effect seems obvious as only a low portion of fertilizer was applied to soil and so can be explained by simple dilution. On the other hand, the soil-acidifying effect of mineral fertilizer (ammonium) is well known (Paul 2007).

Mineral fertilizer had the highest electrical conductivity in comparison to biogas digestate and compost (Table 1). However, this effect was not visible after application to soil (Table 1). After harvest in September 2012, compost-treated soil showed the highest electrical conductivity (Table 1), explainable by a continuous mineralization of compost and thus release of cationic and anionic nutrients contributing to soil electrical conductivity. In the other treatments, highly soluble nutrients contributing to electrical conductivity were probably already leached or taken up by maize plants.

Plant-available nutrients such as K, Ca, Mg, Na and P together with cation exchange capacity were significantly higher in the compost-treated post-harvest soil followed by biogas digestate, fermented biogas digestate and mineral fertilizer (Table 1) in accordance with other studies (Duggan and Wiles 1976; Mays et al. 1973; Weber et al. 2007). Walker and Bernal (2008) reported that the compost treatment did not significantly change soil electrical conductivity or soluble Na, Ca or Mg concentrations. Only soluble K concentration increased, due to a high K content of applied plant material. The total nutrient content of compost is not plant-available immediately after treatment, because of different binding forms within the organic matrix, resulting in a temporal immobilization of nutrients (Fischer and Glaser 2012). Therefore, it is difficult to predict the long-term fertilization behaviour of composts which depend on feedstock materials and composting process (Fischer and Glaser 2012). Hence, compost application prevents the environment from nutrient leaching instead of increasing it as often argued.

Plant-available phosphorus in soil varied between 38 and 63 mg kg^{-1} right after fertilization (Table 1). Fermented biogas digestate and compost revealed significantly higher ($p<0.05$) plant-available phosphorus concentration compared to mineral fertilizer and biogas digestate (Table 1). Plant-available phosphorus concentration in soil after maize harvest varied between 41 and 68 mg kg^{-1} being similar to values right after fertilization (Table 1).

Total N concentration in soil was comparable for all treatments (Table 1). Only compost-treated soil showed significantly ($p<0.05$) higher total N concentration (Table 1). Right after fertilization, plant-available mineral N consisted of less than 50 % of ammonium and more than 50 % of nitrate being highest in mineral fertilizer treatment followed by biogas

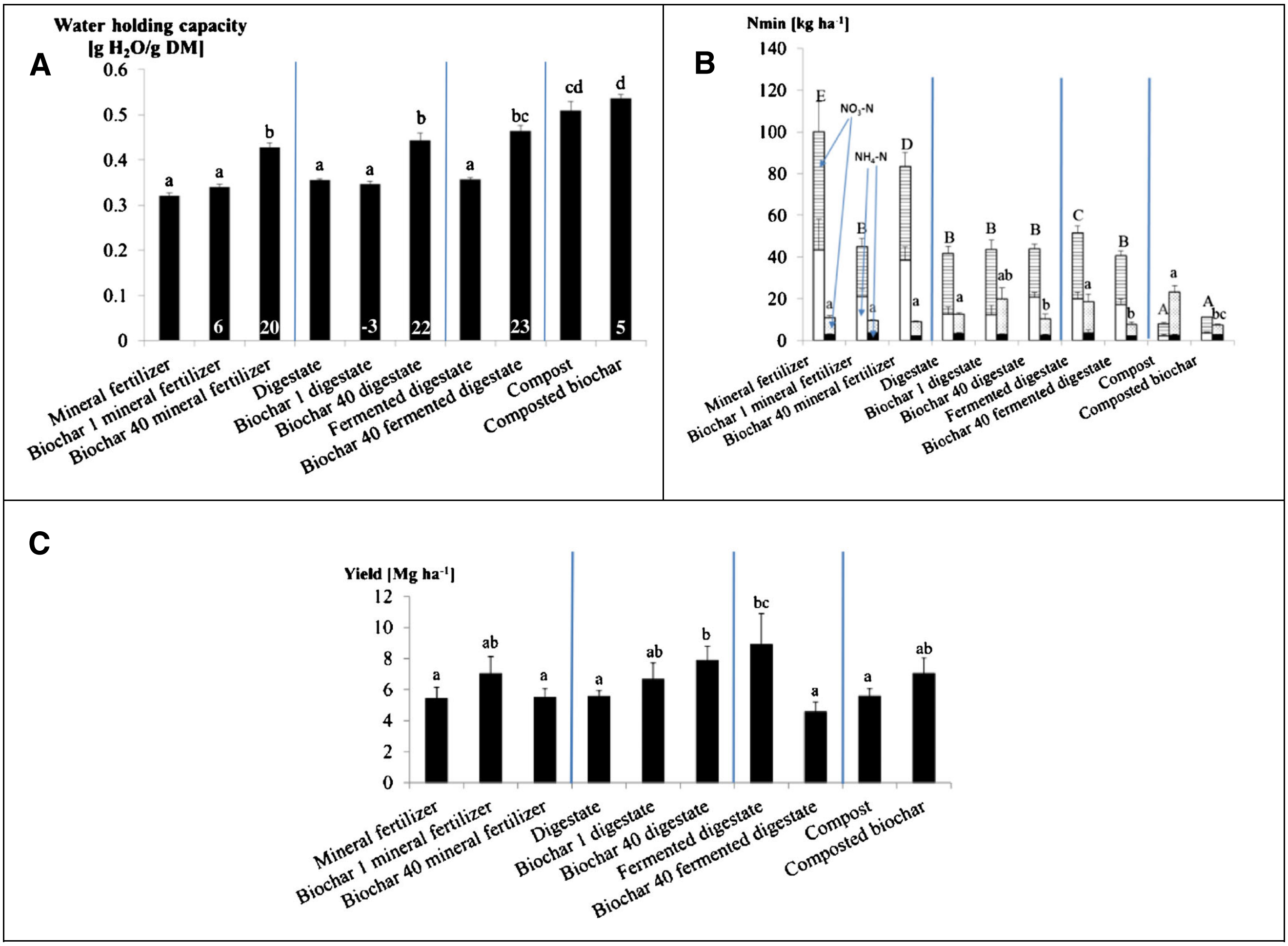


Fig. 2 **a** Water holding capacity of soils amended with fertilizers and biochar; *numbers in bars* represent relative changes compared to corresponding fertilizers without biochar. **b** Plant-available N in soils after fertilization (*left bars*) and harvest (*right bars*). **c** Maize yield in 2012. Given error is standard error (n=5; p<0.05)

digestate and compost (Fig. 2b) despite the fact that all treatments were adjusted to equal mineral N content of 200 kg ha^{-1} (Table 1). The observed discrepancy between theoretical and measured plant-available N concentration (Fig. 2b) could be due to heterogeneity of the mineral fertilizer grains, by volatilization losses during transport and application in the case of biogas digestate and by lower than calculated mineralized N in the case of compost. After harvest, the ratio between ammonium and nitrate remained more or less the same, but concentrations were much lower and more homogeneous compared to soil right after fertilizer application (Fig. 2b). Only fermented biogas digestate and compost showed significantly higher mineral N concentrations after harvest (Fig. 2b). Such can be explained by immobilization of mineral N in the microbial biomass when biogas digestate is fermented. In the case of compost, higher mineral N concentration can be explained by continuous mineralization. Gabrielle et al. (2005) reported annual 3–8 % N mineralization of compost, depending on compost quality and stability. For simplicity reasons, we used 10 % to calculate corresponding compost amounts.

In any case, the mineral N concentration in soil after harvest is low so that a significant N leaching is not very likely after harvest both in fermented biogas digestate and compost treatments. However, it might have occurred before during the vegetation period, which should be the objective of further studies.

3.2 Fertilizer effect on maize yield and nutrient and heavy metal concentrations and uptake

Maize yield was generally low averaging 6–8 Mg ha^{-1} (Fig. 2c) as explained by the late start of the experiment during the vegetation period at the end of May 2012. Maize yield was independent from the type of fertilizer, showing that compost or biogas digestate was as effective as mineral fertilizer for maize growth (Fig. 2c).

Table 1 Basic characteristics of applied fertilizers and soil properties after fertilizer application in May 2012 and after harvest in September 2012

Treatment	pH (H_2O)	EC (μS cm^{-1})	Ca (mmolc kg^{-1})	K (mmolc kg^{-1})	Mg (mmolc kg^{-1})	Na (mmolc kg^{-1})	CEC (mmolc kg^{-1})	PO_4-P (mg kg^{-1})	Total N (g kg^{-1})
Feedstock									
Mineral fertilizer	5.2	160,700	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Biochar 1 mineral fertilizer	6.9	26,100	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	91.8
Biochar 40 mineral fertilizer	9.8	1250	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	14.9
Digestate	8.3	3166	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	33.7
Biochar 1 digestate	10.5	6250	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	50.0
Biochar 40 digestate	9.7	1180	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	10.1
Fermented digestate	6.5	16,970	n.d	n.d	n.d	n.d	n.d	n.d	36.5
Biochar 40 fermented digestate	9.6	1162	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	14.2
Compost	8.8	956	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	11.6
Composted biochar	8.6	882	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	9.9
Biochar	10.2	1000	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	9.6
Soil after fertilizer application									
Mineral fertilizer	6.3±0.2 A	137±19 A	22.5±2.1 B	0.7±0.2 B	2.5±0.2 A	0.4±0.1 A	26.4±1.9 A	40±4 A	0.6±0.3 A
Biochar 1 mineral fertilizer	6.6±0.2 AB	454±53 C	15.2±1.2 A	1.0±0.0 AB	3.0±0.4 A	0.8±0.2 A	20.0±1.7 A	48±4 AB	0.6±0.1 A
Biochar 40 mineral fertilizer	7.6±0.2 C	286±35 B	47.9±5.0 D	10.0±0.8 E	4.6±0.5 B	1.8±0.1 D	61.5±5.0 E	55±3 B	1.0±0.1 B
Digestate	6.7±0.1 B	168±32 AB	24.0±1.2 B	2.1±0.1 B	2.6±0.1 A	0.4±0.0 A	27.8±1.1 B	38±2 A	0.6±0.0 A
Biochar 1 digestate	6.7±0.1 B	127±28 A	19.2±1.9 B	2.3±0.4 B	2.8±0.3 A	0.4±0.0 A	23.5±1.9 A	42±2 AB	0.6±0.0 A
Biochar 40 digestate	7.7±0.3 C	198±30 B	24.4±4.1 B	5.7±0.2 D	5.7±0.2 D	0.7±0.1 B	21.6±5.8 A	52±5 B	1.1±0.3 BC
Fermented digestate	6.4±0.1 B	212±44 AB	28.0±1.4 C	2.4±0.4 B	3.1±0.1 A	0.5±0.1 AB	22.8±6.5 A	52±3 B	0.7±0.1 A
Biochar 40 fermented digestate	7.7±0.3 C	180±35 AB	25.8±1.4 B	4.6±0.3 C	4.0±0.3 B	0.6±0.1 AB	36.1±1.5 C	40±4 A	1.3±0.1 C
Compost	7.1±0.3 C	164±4 AB	23.5±1.4 B	8.7±1.0 E	5.1±0.7 B	1.2±0.1 C	36.5±0.2 C	53±6 B	0.7±0.1 A
Composted biochar	7.5±0.2 C	370±124 BC	32.3±2.2 C	8.2±2.8 E	7.2±1.5 C	1.3±0.4 C	41.5±4.6 C	63±10 B	1.0±0.1 B
Soil after maize harvest									
Mineral fertilizer	6.3±0.3 a	155±11 c	17.0±0.9 a	1.2±0.0 a	3.2±0.1 a	0.6±0.0 b	22.1±2.0 a	45±3 ab	0.7±0.1 a
Biochar 1 mineral fertilizer	6.6±0.3 a	207±16 d	17.9±2.2 a	1.2±0.0 a	3.0±0.2 a	0.3±0.0 a	22.8±2.1 a	44±3 ab	0.6±0.1 a
Biochar 40 mineral fertilizer	6.2±0.3 a	172±12 c	31.5±1.4 c	1.4±0.1 b	4.0±0.3 b	0.7±0.0 b	37.8±1.6 b	45±2 ab	1.2±0.1 c
Digestate	6.6±0.2 a	126±11 b	19.6±0.6 b	1.4±0.1 a	3.0±0.2 a	0.3±0.1 a	24.5±5.2 a	46±2 bc	0.9±0.1 ab
Biochar 1 digestate	6.7±0.3 a	157±14 c	18.9±1.3 ab	1.8±0.2 ab	3.1±0.1 a	0.8±0.0 b	24.7±1.1 a	47±1 bc	0.7±0.0 a
Biochar 40 digestate	6.6±0.3 a	178±21 c	36.1±3.0 d	3.3±0.3 b	4.6±0.1 b	0.5±0.0 b	44.8±2.8 c	41±2 a	1.3±0.1 c
Fermented digestate	6.1±0.2 a	82±6 a	23.1±1.8 b	1.3±0.1 a	4.5±0.2 b	0.4±0.1 a	29.5±3.1 a	49±3 bc	0.8±0.2 ab
Biochar 40 fermented digestate	6.6±0.3 a	259±36 d	44.9±2.6 d	5.5±0.5 c	6.4±0.5 c	0.8±0.1 b	58.0±4.5 d	54±5 c	1.3±0.1 c
Compost	6.5±0.2 a	256±19 d	32.3±1.3 c	17.0±0.7 e	14.8±0.5 e	1.6±0.1 c	65.9±6.1 d	62±5 cd	1.9±0.2 d
Composted biochar	6.9±0.4 ab	311±19 e	38.7±2.1 d	10.3±1.1 d	11.5±1.0 d	1.4±0.2 c	62.1±2.7 d	68±3 d	2.3±0.1 e

Different letters indicate significant differences between means. Upper- and lower-case letters were used to indicate that statistics was done separately for each sampling set; given error is standard error (n=5; p<0.05)

EC electric conductivity, *n.d.* not determined or below detection limit

Microbial inoculation of biogas digestate significantly ($p<0.05$) improved maize growth compared to mineral fertilizer or biogas digestate (Fig. 2c), probably due to temporal N immobilization during microbial inoculation with indigenous microorganisms, although N concentration was highest in minerally fertilized plots (Table 1). Total N uptake into maize plants was comparable for all fertilizers (Fig. 3a). Total N concentration was generally low compared to other studies and comparable to typical N concentration in maize husk (Amoruwa et al. 1987) Total N concentration varied between 9.1 and 13.4 g kg^{-1} and increased in the order biogas digestate, compost, fermented biogas digestate and mineral fertilizer..

Potassium concentration was highest in maize grown on compost-treated soil and lowest in maize grown on mineral fertilizer (Table 2). No fertilizer effects on maize P, Mg and micronutrient concentrations could be observed apart from Cu (Table 2). Fertilization with biogas digestate led to highest P uptake by maize plants. Mineral fertilization and biogas digestate led to higher Ca uptake by maize plants (Fig. 3). Potassium

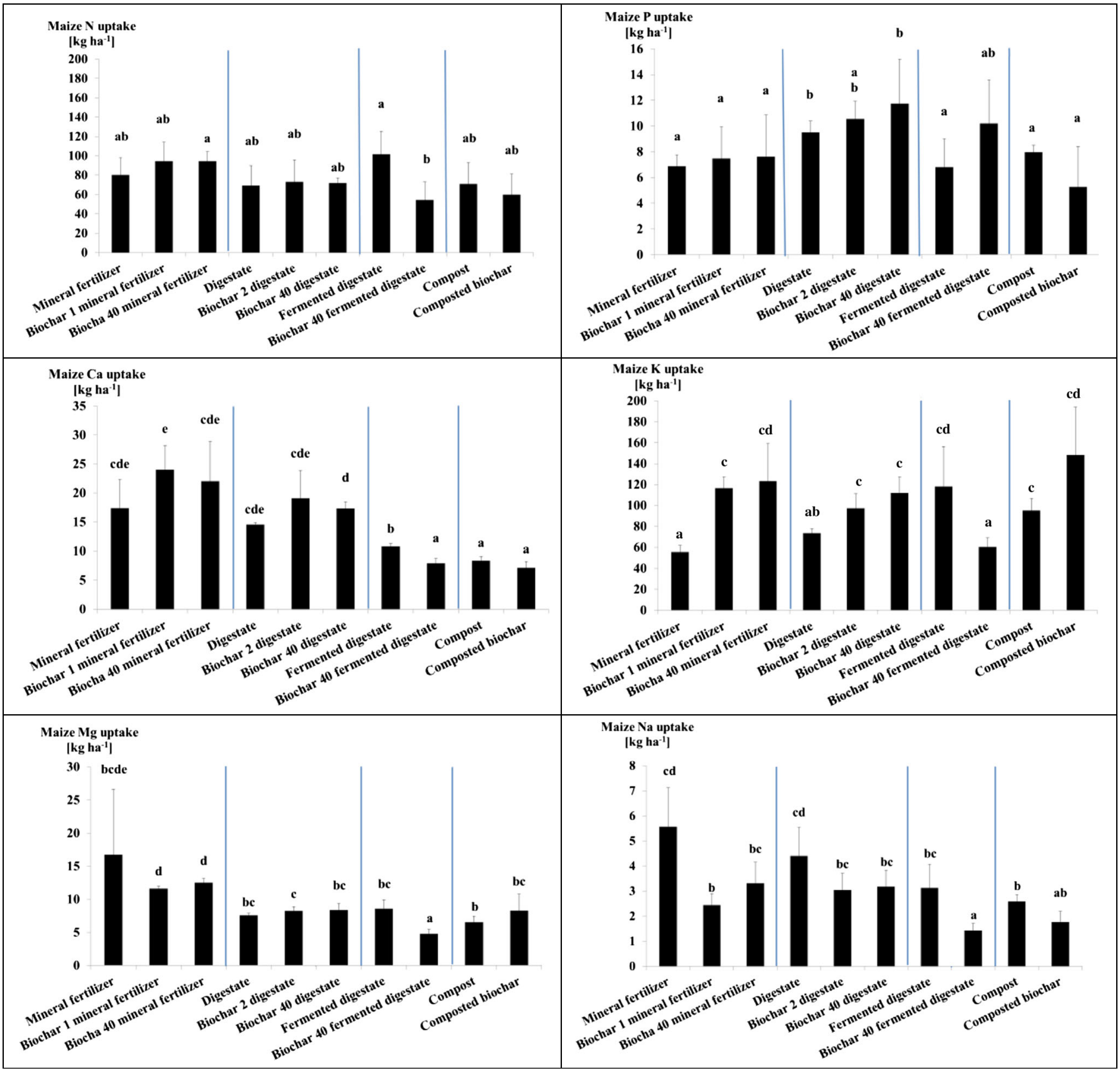


Fig. 3 Uptake of major nutrients into total above-ground biomass of maize. *Different letters* indicate significant differences between means; given error is standard error ($n=5$; $p<0.05$)

Table 2 Macro- and micronutrient and heavy metal concentrations of maize plant

Fertilizer	Total N (g kg^{-1})	P (g kg^{-1})	K (g kg^{-1})	Mg (g kg^{-1})	Ca (g kg^{-1})	Na (g kg^{-1})	Mn (mg kg^{-1})	Cu (mg kg^{-1})	Ni (mg kg^{-1})	Zn (mg kg^{-1})	Co (mg kg^{-1})	Cr (mg kg^{-1})	Pb (mg kg^{-1})	Cd (mg kg^{-1})
Mineral fertilizer	12.7±0.6 d	1.4±0.2 a	10.3±0.6 a	1.2±0.1 a	3.6±0.7 d	1.20±0.23 d	322±31 ab	54.3±8.8 d	11.7±4.7 bc	128±12 b	1.6±0.8 ab	282±101 b	10.2±1.5 b	0.48±0.14 ab
Biochar 1 mineral fertilizer	13.4±0.6 d	1.4±0.2 a	12.1±0.3 b	1.5±0.1 b	3.4±0.2 d	0.34±0.02 a	777±134 c	34.7±3.3 b	3.6±0.8 a	145±12 bc	0.9±0.1 a	126±32 a	6.4±0.6 a	0.63±0.03 b
Biochar 40 mineral fertilizer	13.4±0.3 d	2.1±0.1 b	16±3 c	1.9±0.4 b	3.1±0.5 d	0.46±0.04 b	378±64 b	36.7±2.2 b	7.8±1.0 b	155±10 c	1.3±0.2 b	151±46 ab	8.9±1.0 b	0.65±0.04 b
Digestate	9.3±0.3 a	1.6±0.1 a	13.1±0.5 bc	1.3±0.1 a	2.5±0.1 c	0.76±0.19 c	311±26 ab	41.3±2.0 c	11.3±3.2 bc	95±7 a	1.1±0.2 ab	205±37 b	10.9±1.1 b	0.50±0.13 ab
Biochar 1 digestate	9.2±0.4 a	1.4±0.1 a	11.9±0.8 b	1.3±0.1 a	2.5±0.2 c	0.39±0.04 ab	274±23 a	32.6±1.9 ab	3.4±1.1 a	93±8 a	0.7±0.0 a	80±11 a	11.8±2.3 b	0.52±0.13 ab
Biochar 40 digestate	9.1±0.5 a	2.0±0.2 b	17.4±1.8 c	1.1±0.2 a	1.8±0.2 b	0.46±0.03 b	339±26 ab	34.3±1.9 b	3.6±0.5 a	137±10 bc	0.9±0.2 ab	84±17 a	11.2±1.8 b	0.48±0.13 a
Fermented digestate	11.4±0.8 c	1.6±0.1 a	13.1±0.2 b	1.2±0.1 a	1.9±0.2 b	0.40±0.04 ab	276±34 a	33.4±2.2 b	15.0±3.0 c	128±16 b	1.1±0.1 b	67±6 a	9.4±0.7 b	0.65±0.02 b
Biochar 40 fermented digestate	9.2±0.2 a	1.6±0.1 a	14.8±1.7 b	1.2±0.2 a	1.9±0.1 b	0.33±0.04 a	332±24 ab	36.6±3.8 b	3.4±1.1 a	148±16 bc	0.6±0.3 a	122±46 a	6.2±0.8 a	0.26±0.16 a
Compost	10.2±0.4 bc	1.4±0.1 a	18.2±0.3 c	1.2±0.1 a	1.5±0.1 a	0.47±0.06 b	320±41 ab	28.8±2.3 a	7.0±3.0 ab	116±4 b	0.8±0.1 a	88±32 a	6.4±0.5 a	0.67±0.02 b
Composted biochar	9.6±0.4 ab	1.4±0.2 a	13.9±1.9 b	1.3±0.3 a	1.4±0.2 a	0.32±0.03 a	255±17 a	23.1±5.7 a	4.8±2.3 a	131±29 abc	0.7±0.2	84±6 a	8.5±1.2 b	0.48±0.15 a

Different letters indicate significant differences between means. Given error is standard error ($n=5$; $p<0.05$)

uptake by maize was lowest after biogas and mineral fertilization (Fig. 3). Potassium and micronutrient (Mn, Cu, Zn) concentrations in the maize plants were generally higher, and P, Ca and Mg concentrations were comparable with the data reported by Amoruwa et al. (1987).

3.3 Biochar effects on soil properties

In this study, maize was not irrigated in order to verify and differentiate the effects of fertilizers with and without biochar on yield and plant nutrition under natural weather conditions during the growing season in 2012. Already, 1 Mg ha^{-1} of biochar increased the water holding capacity of the sandy soil under study by 6 % and 40 Mg ha^{-1} of biochar by up to 25 % (Fig. 2a). Karhu et al. (2011) showed that 9 Mg ha^{-1} of biochar increased water holding capacity by 11 % in silty loamy soil. Liu et al. (2012) demonstrated that 20 Mg ha^{-1} biochar addition to a sandy soil increased plant-available water holding capacity by 100 %, helping to balance fluctuations in plant-available water during the growing cycle and to increases in irrigation efficiency.

One and 10 Mg ha^{-1} biochar additions slightly increased pH, while 40 Mg ha^{-1} biochar addition significantly ($p<0.05$) increased soil pH values right after fertilizer application; this effect was being levelled out after maize harvest (Table 1). Biochar addition of at least 10 Mg ha^{-1} significantly ($p<0.05$) increased plant-available K and Mg concentrations in soil, but not Ca when biochar was combined with biogas digestate (Table 1). After maize harvest, concentrations of plant-available cations and differences among different fertilizers were comparable to values directly after fertilization (Table 1). After maize harvest, exchangeable Ca and K concentrations were significantly higher ($p<0.05$) when at least 10 Mg ha^{-1} biochar was applied (Table 1). Liu et al. (2012) reported significantly higher plant-available K concentrations in a sandy soil in north-eastern Germany after 20 Mg ha^{-1} biochar and 30 Mg ha^{-1} compost application compared to the same amount of compost alone. However, plant-available Ca, Mg, Al, Na and P were not significantly influenced by biochar additions in the study of Liu et al. (2012).

Biochar addition of at least 10 Mg ha^{-1} significantly ($p<0.05$) increased cation exchange capacity in all treatments apart from biogas digestate (Table 1). The same result plus a positive biochar effect on biogas digestate was observed after maize harvest (Table 1). Cation exchange capacity of biochar is closely related to surface functional groups such as phenolic OH and carboxylic groups (Liu et al. 2013) but varies with feedstock and combustion conditions (Wiedner et al. 2013). Increase in surface functional groups is a natural process of the ageing of biochar in soil (Glaser et al. 2000). In addition, ash content and pH value influences cation exchange capacity when determined at soil-inherent pH as in our study. Therefore, an increase of cation exchange capacity after biochar addition is due to the input of ash adhering to the biochar surface. The still higher cation exchange capacity of biochar-amended treatments after maize harvest might be due to biochar surface oxidation generating negatively charged oxygen-containing carboxyl, hydroxyl and phenolic surface functional groups (Atkinson et al. 2010; Uchimiya et al. 2011). Therefore, one has a real increase of cation exchange capacity as reported in previous studies (Glaser et al. 2002; Yamato et al. 2006; Van Zwieten et al. 2007). Such is corroborated by the fact that, apart from a few exceptions, exchangeable cations in soil after harvest to which biochar was applied were significantly higher compared to corresponding fertilized soils without biochar (Table 1). At the same time, pH values in soil after harvest were comparable for all treatments (Table 1).

Biochar addition of at least 10 Mg ha^{-1} significantly ($p<0.05$) increased total N concentration in soil (Table 1). Biochar-treated soils with more than 10 Mg ha^{-1} exhibited significantly ($p<0.05$) higher total N concentration compared to corresponding treatments without biochar even after one vegetation period (Table 1). Biochar addition significantly ($p<0.05$) reduced N from ammonium and nitrate when combined with mineral fertilizer and fermented biogas digestate (Fig. 2b). In all other treatments, plant-available N concentration was not significantly influenced by biochar application, in agreement with previous studies demonstrating minor effects of biochar on N from ammonium and nitrate in soil (DeLuca et al. 2006; Jones et al. 2012; Kolb et al. 2009). However, plant-available N of composted biochar was lower than N from compost without biochar after harvest (Fig. 2b), indicating that increased microbial activity immobilized mineral N. A decreased microbial activity after biochar addition is also possible but not very likely because the C/N ratio of compost of 10 was very low and, even after biochar addition, it was only 17.

Biochar application generally increased plant-available P concentration in soil, being significant ($p<0.05$) when combined with mineral fertilizer and biogas digestate at 40 Mg ha^{-1}. Biochar combined with fermented biogas digestate significantly decreased ($p<0.05$) plant-available P concentration in soil (Table 1).

3.4 Biochar effect on maize yield

Biochar addition of 1 Mg ha^{-1} to mineral fertilizer and biogas digestate increased maize yield by 20 and 30 %, respectively (Fig. 2c). Addition of 10 Mg ha^{-1} biochar to compost increased maize yield by 26 % compared to pure compost (Fig. 2c). Addition of 40 Mg ha^{-1} biochar to biogas digestate increased maize yield by 42 % ($p<0.05$) but reduced maize yield by 50 % ($p<0.05$) when biogas digestate was fermented together with biochar (Fig. 2c). Addition of 40 Mg ha^{-1} biochar did not affect maize yield when combined with mineral fertilizer (Fig. 2c). Little is known on comparable field experiments. Schulz and Glaser (2012) reported similar results of a greenhouse study using a sandy soil and biochar combined with mineral fertilizer and compost. Uzoma et al. (2011) showed that the application of 20 Mg ha^{-1} to a sandy soil limited maize height and total biomass in contrast to 15 Mg ha^{-1} biochar application rate in a greenhouse experiment. Major et al. (2010) reported no significant increase of maize yield in the first year of a field trial in a Colombian savanna Oxisol when 8 and 20 Mg ha^{-1} biochar had been applied without additional fertilizer. In the following 2 years, however, maize yield increased with increasing biochar application rate (Major et al. 2010). Our experiment clearly revealed positive biochar effects on maize yield when combined with organic fertilizers and shows that low amounts of biochar (1 Mg ha^{-1}) can improve mineral fertilizer efficiency.

3.5 Biochar effect on maize nutrients and heavy metal concentrations and their total uptake into maize plants

Biochar influenced uptake of P, K, Mg and Zn into maize plants. High amounts of biochar addition increased significantly P concentration in maize when combined with mineral fertilizer or biogas digestate (Table 2). Total P uptake to maize biomass was only increased by tendency (Fig. 3). Lehmann et al. (2003) reported a significantly higher P uptake into cowpea (*Vigna unguiculata*) when biochar was combined with mineral fertilizer or manure or a combination of both in a Ferralsol and in Terra Preta. Uzoma et al. (2011) reported 2–6 kg ha^{-1} higher P uptake into maize grain when 10–20 Mg ha^{-1} biochar was applied.

Biochar addition increased significantly ($p<0.05$) Mg concentration in maize when combined with mineral fertilizer but had no effect on all other fertilizers (Table 2). Also, Mg uptake by maize plants was more or less equal for all treatments (Fig. 3). Uzoma et al. (2011) reported about 2 kg ha^{-1} higher Mg uptake by maize grain when at least 15 Mg ha^{-1} biochar was applied. Lehmann et al. (2003) reported a lower Mg uptake by cowpea grown on Ferralsol or Terra Preta when mineral or organic fertilizers were applied with and without biochar.

Biochar addition to mineral and organic fertilizers increased both K concentration (Table 2) and uptake

(Fig. 3) in maize. Also, Lehmann et al. (2003) reported a positive biochar effect on K uptake into cowpea grown on a Ferralsol, but not when grown on Terra Preta. Uzoma et al. (2011) reported about 10 kg ha^{-1} higher K uptake into maize grains when 15–20 Mg ha^{-1} biochar was applied.

Biochar addition increased significantly ($p<0.05$) Zn concentration in maize in all investigated treatments (Table 2). Also, Lehmann et al. (2003) reported higher Zn uptake into cowpea grown on a Ferralsol when biochar was added.

No biochar effects were observed for N, Ca, Mn, Co, Cr and Pb uptake by maize plants. Biochar addition did not change N concentration and uptake by maize apart from combination with microbially inoculated biogas digestate, which reduced significantly ($p<0.05$) maize N concentration (Table 2) and uptake (Fig. 3). Lehmann et al. (2003) reported reduced N uptake by cowpea when biochar was applied together with mineral fertilizer or manure or a combination of both to a Ferralsol in comparison to the fertilizers applied without biochar. Also for Terra Preta, a reduced N uptake into cowpea was observed even when mineral fertilizer or manure or a combination of both was applied in comparison to a Ferralsol receiving the fertilizers (Lehmann et al. 2003). Kammann et al. (2011) also observed reductions in foliar N concentrations in a pot trial with a relatively nutrient-rich peanut hull biochar, but in this case, the reduction resulted likely from increased N use efficiency since the authors reported biomass increases of up to 60 %. Uzoma et al. (2011) reported 30 kg ha^{-1} higher maize grain N uptake when at least 15 Mg ha^{-1} biochar was added. Van Zwieten et al. (2010) found a positive biochar N interaction for wheat grown in the greenhouse.

Biochar addition did not change Ca concentration (Table 2) or uptake (Fig. 3) in maize in most cases. Uzoma et al. (2011) reported about 0.5 kg ha^{-1} higher Ca uptake by maize grain when at least 15 Mg ha^{-1} biochar was added. Lehmann et al. (2003) reported a higher Ca uptake by cowpea when biochar was combined with mineral and/or organic fertilizers in a Ferralsol or applied to Terra Preta.

Lower uptake of Na, Cu and Ni and Cd by maize plants was observed after biochar addition. Biochar addition reduced significantly ($p<0.05$) Na concentration of maize in all treatments (Table 2). As Na is an antagonist to K, such might be due to enhanced K uptake by maize.

Biochar reduced significantly ($p<0.05$) Cu concentration in maize when applied together with mineral fertilizer and biogas digestate, but not when applied together with fermented biogas digestate or compost (Table 2). Biochar addition decreased significantly ($p<0.05$) Ni concentration in maize plant independent from fertilizer type (Table 2). Biochar addition decreased significantly ($p<0.05$) Cd concentration in maize when combined with fermented biogas digestate or compost (Table 2).

Explanations for the discrepancies between our results and literature data (especially the study of Lehmann et al. 2003) might be the use of different plants and experimental setups. In the study of Lehmann et al. (2003), pots were used in which the substrates were homogeneously mixed, while our study was a field study in which biochar and fertilizers were mixed only to 15 cm soil depth while plant roots could reach a depth of 1 m or even more. Therefore, roots are less affected by biochar due to the low incorporation depth (Jones et al. 2012). Furthermore, the capability of biochar to increase nutrient retention (e.g. Laird et al. 2010; Knowles et al. 2011) might be a limiting factor for nutrient availability of deep-rooting plants, because nutrient layers do not penetrate to deeper soil layers.

Biochar addition to soil can affect physico-chemical and biological processes such as adsorption and desorption, complexation/dissociation, oxidation/reduction and mobilisation/immobilization (He et al. 2005; Park et al. 2011; Uchimiya et al. 2011) that control mobility and availability of macro- and micronutrients for plants. Such have direct effects on plant nutrient uptake and indirect effects on crop yield. Therefore, these complex interactions led to different biochar effects on maize nutrient concentrations (Table 2) and uptake (Fig. 3), depending on biochar amount and type of co-applied fertilizer. Further studies are required to trace specifically soil-water-plant interactions of biochar and nutrients or heavy metals.

4 Conclusion

The objective of this study was to evaluate the short-term effects of biochar in combination with agronomically relevant inorganic and organic fertilizers on soil properties, plant nutrition and yield in a sandy soil under field conditions in Northern Germany. The first year of this field trial has shown that high application rates of biochar significantly increased water holding capacity. High doses of biochar in combination with fertilizers increased maize yield compared to corresponding pure organic fertilizer applications. As expected, low biochar amounts such as 1 and 10 Mg ha^{-1} had only minor effects on water holding capacity and soil and plant properties. However, low biochar amounts of 1 Mg ha^{-1} increased significantly the mineral fertilizer efficiency, indicating that the application of economically sustainable amounts of biochar may become an option for the industrial agriculture in temperate regions. The addition of biochar to the composting processes improved significantly the resulting compost in regard to its effect on maize yield. With respect to plant nutrition, higher P, K, and Zn; more or less equal N, Mg, Ca, Mn, Co, Cr and Pb; and lower Na, Cu, Ni and Cd uptake by maize plants could be observed when biochar was added compared to corresponding fertilizers without biochar. Biochar effects on soil properties, plant nutrition and growth are highly complex and differ significantly in combination with mineral or organic fertilizers. More process-based research is needed to understand the biochemical interactions in soil after biochar application in order to optimize complex biochar fertilizers for field application. Nevertheless, our field study clearly showed no negative effects of biochar. Instead, our complex biochar-fertilizer combinations clearly demonstrated at least equality with conventionally applied pure mineral fertilizer with respect to yield and plant nutrition. Therefore, biochar has the potential to increase agronomic performance even in temperate regions, especially when combined with organic fertilizers. Furthermore, field trials have shown that biochar effects on plants and soil properties differ to studies performed under laboratory or greenhouse conditions. Therefore, long-term biochar field trials under various conditions are needed urgently in order to assess the long-term effects of biochar on soil properties and plant growth in realistic agricultural ecosystems.

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